THEORETICAL CHEMISTRY INSTITUTE
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HYPERVIRIAL THEOREMS AND THE HELLMANN-FEYNMAN
THEOREM IN DIFFERENT COORDINATE SYSTEMS

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WIS-TCI-78 12 February 1965

MADISON, WISCONSIN [redacted]

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THEOREM IN DIFFERENT COORDINATE SYSTEMS*

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Abstract

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It is shown that the difference between the Hellmann-Feynman theorems in two different coordinate systems is in general a hypervirial theorem. Author

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*This research was supported by the following grant: National Aeronautics and Space Administration Grant NsG-275-62.

Recently[1-4] there has been considerable interest in the fact that the Hellmann-Feynman theorem takes different forms depending on the coordinate system one uses. Thus if we are using coordinates x_k and if λ is a parameter then the (generalized) Hellmann-Feynman theorem may be written

$$E' = (\psi_x, H_x' \psi_x)$$

where we have denoted differentiation with respect to λ by a prime and where the subscript x on ψ and H is to remind us that they are the wave function and Hamiltonian appropriate to the x_k coordinate system. Similarly if we use coordinates y_k we have

$$E' = (\psi_y, H_y' \psi_y)$$

from which we infer that

$$(\psi_y, H_y' \psi_y) - (\psi_x, H_x' \psi_x) = 0. \qquad (1)$$

For the example discussed in references 1-3 eq. (1) has been found to be the virial theorem. In the example discussed in reference 4 eq. (1) is found to be again of a similar form. It is the purpose of this note to show that in general eq. (1) is a hypervirial theorem.[5] To do this we assume[6] that the transformation from the x_k

system to the Y_K system can be accomplished by means of a unitary transformation[7-8]

$$\Psi_Y = U \Psi_x \tag{2}$$

$$H_Y = U H_x U^+ \tag{3}$$

From this it follows that

$$H_Y' = U' H_x U^+ + U H_x' U^+ + U H_x U^{+\prime} \tag{4}$$

We now make use of $U^+U = 1$ to find

$$U^{+\prime} U + U^+ U' = 0$$

Using this eq. (4) becomes

$$H_Y' = U \left(H_x' + (U^+U', H_x) \right) U^+$$

Thus using eq. (2), eq. (1) may be written

$$(\Psi_x, (U^+ U', H_x) \Psi_x) = 0 \tag{5}$$

which <u>is</u> the hypervirial theorem for $U^+ U'$.

To write down a general formula for $U^{+}U'$ would be quite complicated. However for the examples discussed in references 1-4 it is sufficient (see footnote 6) to consider simple scalings $X_k = \lambda Y_k$. For this case it is known (see for example reference 8a) that

$$U^{+}U' = \frac{i}{2\hbar\lambda}\sum_{k=1}^{s}(p_k x_k + x_k p_k)$$

where p_k is the momentum canonically conjugate to x_k, and where we have scaled s coordinates. When inserted into eq. (5) this yields the results which we have already mentioned, though it is by no means the simplest way of deriving them.

Footnotes and References

1. C. A. Coulson, and A. C. Hurley, J. Chem. Phys., 37, 448 (1962).
2. P. Phillipson, J. Chem. Phys., 39, 3010 (1963).
3. A. C. Hurley in Molecular Orbitals in Chemistry, Physics and Biology, P. Löwdin and B. Pullman, ed. (Academic Press, New York, 1964).
4. M. L. Benston, Bull, A.P.S., 10, 102 (1965).
5. J. O. Hirschfelder, J. Chem. Phys., 33, 1762 (1960).

6. Since this assumption implies that X_k and Y_k have the same range of values it would appear that the subsequent analysis will have restricted applicability. Happily this is not the case. Namely our analysis also applies to any coordinates Z_k which are λ-independent functions of the Y_k since this will mean that the Hellmann-Feynman theorem takes the same form in the Z_k and Y_k coordinate systems.

7. M. Born, W. Heisenberg, and P. Jordan, Zsf. Phys., 35, 557 (1926).
8. P. Jordan, Zsf. Phys., 37, 383 (1926), 38, 513 (1926).
9. See also (a) S. T. Epstein, and J. O. Hirschfelder, Phys. Rev., 123, 1495 (1964) and (b) M. Eger and E. P. Gross, Annals of Phys., 24, 63 (1963).